Indian J. Phys. **80** (4), 397-399 (2006)

Note

Phonons behavior in ternary chalcogenide mixed spinel

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Received 29 August 2005, accepted 22 November 2005

Abstract : In recent years, various studies of electrical, magnetic and vibrational properties of mixed spinels have been reported which are interesting both practically and theoretically. In the present note we have developed a theoretical model and interpreted the concentration-dependence of lattice vibration frequencies of $CdCr_2Se_{4(1-x)}$ and $Zn_{1-x}Hg_xCr_2Se_4$. We find an overall good agreement between theoretical and experimental data

Keywords : Ternary chalcogenide mixed spinel, phonon behaviour, concentration dependence, theoretical model

PACS No. : 63.20.-e

In the past few decades, various studies of electrical, magnetic and vibrational properties of mixed spinels have been reported which are interesting from both the theoretical and experimental points of view [1-3]. The study of long wavelength optical lattice vibrations of mixed systems with many atoms in the unit cell, is important for understanding the disorder effect in matter [4-6]. These lattice imperfections have large effect on most of the physical properties of the crystals. In particular, these defects significantly change the dynamics of the crystal lattice. Such changes are often sufficient to allow interaction with light radiation in cases where it could not otherwise occur. Thus, presence of small impurities may make a periodic solid, spectroscopically interesting and informative. Due to these interesting properties, theoretical models have been proposed in recent years to account for different types of mode behaviour in different types of mixed spinel systems.

Wakamura *et al* [7,8] explained the compositional dependence of the vibrational modes of $Hg_xZn_{1-x}Cr_2Se_4$ and $Zn_{1-x}Cd_xCr_2S_4$ mixed spinel systems, which include basic units in which the force parameters and atomic masses of the substituted atoms varying monotonically with the composition, are taken into consideration. Bruesch and Ambrogio [9] presented an analysis of the observed IR and Raman-active phonons of $CdCr_2S_4$ and $CdCr_2Se_4$, based on the simple force model with four adjustable short-range parameters. Watanabe *et al* [10] used the above force model to explain the lattice vibrations of the $Cd(In_{1-x}Cr_2S_4)$ mixed system.

In the present note, we have developed a model to study the phonons in the spinel structure compounds at the zone-centre as a function of composition and plot a graph between composition and calculated frequencies. We find an overall good agreement between experimental and theoretical results.

Crystal structure and dynamical model :

The spinel structure compounds crystallize in space group $Fd3m(O_h)$. The unit cell of normal spinel AB_2C_4 contains 14 atoms and the symmetry of the vibrational modes at the Γ-point is represented by

$$\Gamma = A_{1g} + E_g + 2E_u + 2A_{2u} + F_{1g} + 3F_{2g} + 5F_{1u} + 2F_{2u}, \quad (1)$$

where $5F_{1u}$ contains the four infrared-active optical modes and one acoustic mode, and A_{1g}, E_g, and $3F_{2g}$ are the Raman-active modes. Rest of the modes is Raman-inactive (F_{1g}) and infrared-inactive ($2E_u$, $2A_{2u}$, $2F_{2u}$) modes.

The potential energy of the compounds possessing the spinel structure is expressed as :

$$\Phi = \phi^N + \phi^C + \phi^I + \phi^M, \quad (2)$$

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where superscripts N and C refer to the non-Coulombic and Coulombic parts, respectively. I and M stand for contributions corresponding to dipole interaction and macroscopic field, respectively.

The secular determinant is given by

$$D(q, kk') - \omega^2 \delta_{\alpha\beta}\, \delta_{kk'} \Big| = 0\,, \tag{3}$$

where $kk' = 1, 2, \ldots\ldots$ s are the labelings of the ions per unit cell. q denotes the wave vector whose allowed values range over the first Brillouin zone. α and $\beta = x,y,z$ designating the coordinate axes and δ is the usual Kronecker delta symbol. mk is the mass of the ion k in the lm_kth cell. The elements of the dynamical matrix are defined as

$$D_{\alpha\beta}(q\ kk') = \sum_{l} \frac{1}{\sqrt{m_k m_k}} \phi_{\alpha\beta}(lK, l'k') \exp\left[iq.r^0(lK, l'k')\right], \tag{4}$$

where $r^0(lK, l'k') = r^0(l'k') - r^0(lK)$. As usual, $\phi_{\alpha\beta}(lK, l'k')$ denotes the coupling parameters between ions (lk) and $(l'k')$.

It has been observed that the contributions due to the second term, *i.e.*, the long-range Coulombic interaction on the force constants have been neglected because these long-range Coulombic interactions, have no effect on the modes at Γ. Also contributions of the third term (dipole interactions) and the last term (the macroscopic field part) are negligibly smaller in comparison with the non-Coulombic parts in the zone-center frequency calculations in for spinel structure.

For the non-Coulombic interactions, the potential energy of the spinel structure using Taylor's series can be written as

$$\Phi^N = \sum_{lmn} \frac{1}{} \left(\frac{d\phi^N}{dr} \right. \qquad r^0_{lmn}(S_{lmn} - S_0) + \frac{1}{2} |S_{lmn} - S_0$$

$$+ \frac{1}{2} \left\{ \frac{1}{r} \frac{d}{dr} \left(\frac{1}{r} \frac{d\phi}{dr} \right) \right\}_{|r|=r_i} \left\{ r^0_{lmn}(S_{lmn} - S_0) \right\}^2 \tag{5}$$

where S_0 and S_{lmn} are the displacements of the central ion and its first neighbor ions from their normal positions, r_{lmn} represents the position coordinates of neighboring ions in equilibrium. l, m, n, represent the direction cosines of the line joining the central ion and a nearest neighbors. $|r_1|$ is the nearest neighbor distance. In this note, we have considered the non-Coulombic interaction between central ion and its three nearest neighbors.

Let A_k be the bond-stretching force constant defined by the second derivative of the potential energy ϕ^N as

$$\frac{e^2}{V} A_k = \frac{d^2\phi^N}{dr^2}_{|r|=|r_k|} \tag{6}$$

The bond-bending force constant B_k is expressed as the first derivative of the potential energy ϕ^N as

$$\frac{e^2}{V} B_k = \frac{1}{r} \frac{d\phi^N}{dr}_{|r|=|r_k|}$$

Here, $k = 1, 2, 3$ for first, second and third neighbor

The mixed spinel resulted into two spinel compounds at composition $x = 0$ and $x = 1$. These are called end members of the mixed spinel. We have solved 42 x 42 dynamical matrix at the zone-centre and find out the force constants for the end members $CdCr_2Se_4$, $CdCr_2S_4$, $ZnCr_2Se_4$ and $HgCr_2Se_4$ with the help of the measured phonon frequencies of A_{1g}, E_g and F_{1u} modes which is given in Table 1. The calculated force constants are given in Table 2. The force constants and masses of the mixed spinels at

Table 1. Measured [7,8] zone center phonon frequencies (cm^{-1}) of $CdCr_2Se_4$, $CdCr_2S_4$ $ZnCr_2Se_4$ and $HgCr_2S_4$ used as input data

Species	Measured data			
	$CdCr_2Se_4$	$CdCr_2S_4$	$ZnCr_2Se_4$	$HgCr_2Se_4$
A_{1g}	237	394	240	237
E_g	154	256	152	157
$F_{1u}(1)$	288	380	297	286
$F_{1u}(2)$	267	324	274	268
$F_{1u}(3)$	186	240	198	169
$F_{1u}(4)$	75	95	85	55

Table 2. The values of force constants (kdynes/cm)

Force parameters	$CdCr_2Se_4$	$CdCr_2S_4$	$ZnCr_2Se_4$	$HgCr_2Se_4$
A_1	49 74	46.96	54.14	54 14
B_1	2 93	1.50	1.44	1 44
A_2	74.41	80.95	78.23	78 23
B_2	4.75	1.69	4.12	4 12
A_3	14 33	18.25	14.70	14 70
B_3	1 08	0.31	1.61	1 61

different compositions ($0 < x < 1$) evaluated using Vegard's law [11]. The force constants and the mass of the substituted atoms are as

$$A_{CdCr2Se4(1-x)S4x} = 4(1-x) A_{CdCr2Se4} + 4x A_{CdCr2S4}\,,$$

$$M_{CdCr2Se4(1-x)S4x} = 4(1-x) M_{CdCr2Se4} + 4x M_{CdCr2S4}\,,$$

for $CdCr_2Se_{4(1-x)}S_{4x}$ and for $Zn_{1-x}Hg_xCr_2Se_4$,

$$A_{Zn1-xHgxCr2Se4} = (1-x)\ A_{ZnCr2Se4} + x A_{HgCr2Se4}.$$

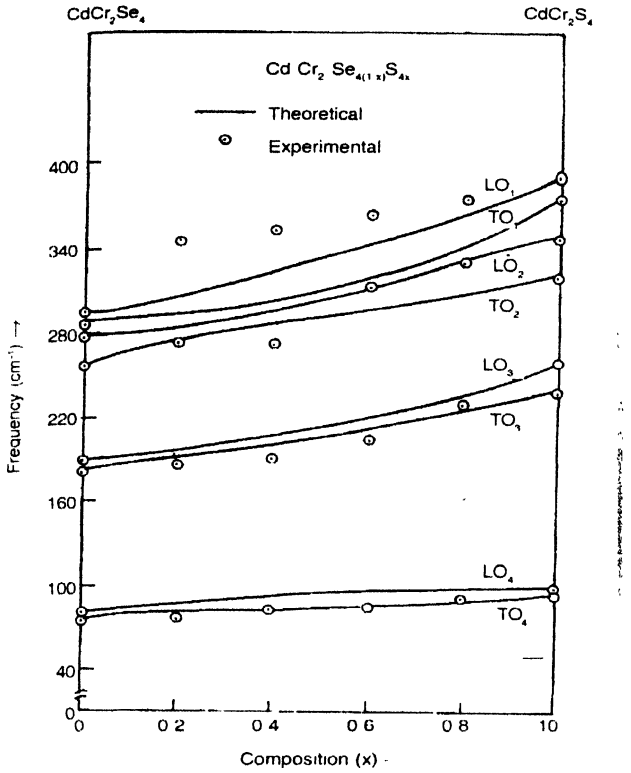

Figure 1. One mode behaviour in the mixed spinel $CdCr_2Se_{4(1-x)}S_{4x}$

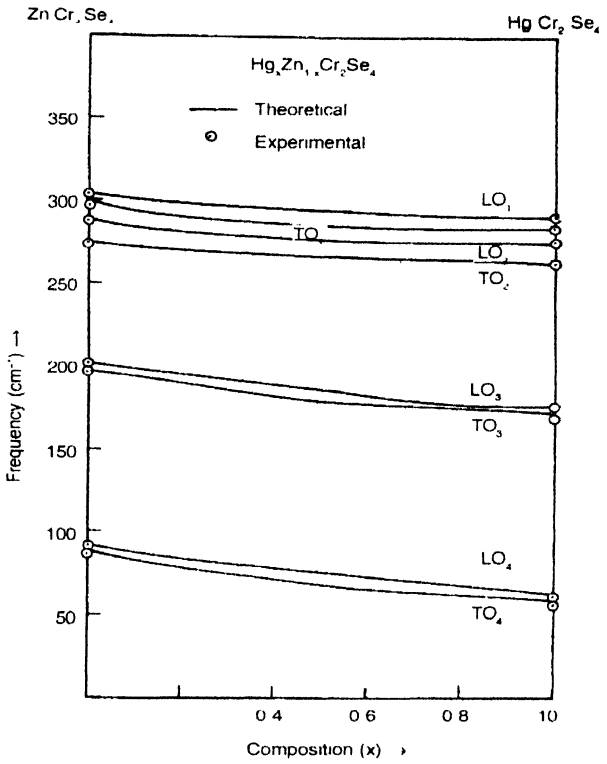

Figure 2. One mode behaviour in the mixed spinel $Zn_{1-x}Hg_xCr_2Se_4$

$$M_{Zn1-xHgxCr2Se4} = (1-x)M_{ZnCr2Se4} + xM_{HgCr2Se4}.$$

Using these relations, the force constants and masses for different compositions, the phonon frequencies are calculated at the zone centre. Results are shown in Figures 1 and 2 along with the available experimental results which exhibit an overall good agreement for all values of composition. It is clear from the figures that there is one set of optical phonon frequencies for whole composition range, *i.e.*, one mode behavior.

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